

PATENT SPECIFICATION

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 (72) Inventors JAMES McNIVEN COURTNEY, THOMAS
 GILCHRIST and WILLIAM McCLEMENTS
 MUIR



(54) A METHOD OF MODIFYING THE PROPERTIES OF A POLYMER

(71) We, THE UNIVERSITY OF STRATHCLYDE, a British University incorporated by Royal Charter, of 204 George Street, Glasgow G1 1XW, Scotland, Great Britain, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of modifying the properties of a polymer. It is particularly suitable where the polymers are in the form of a membrane or film to be used in membrane separation processes such as ultrafiltration, direct or reverse osmosis or dialysis.

"Dialysis" is the passage of a solute through a membrane under the driving force of a concentration gradient.

"Ultrafiltration" principally involves the transfer of solvent through a membrane under the driving force of a pressure gradient.

"Direct osmosis" is the passage of solvent through a membrane from a relatively less concentrated to a more concentrated solution.

"Reverse osmosis" occurs when a pressure exceeding the osmotic pressure is applied to the more concentrated solution to reverse the flow of solvent, i.e. to transfer solvent from the more concentrated to the less concentrated solution.

Commercial dialysis membrane based on regenerated cellulose films cannot be heat-sealed and the available methods of modifying permeability for a given membrane thickness involve stretching, swelling or leaching-out processes.

Commercial ultrafiltration and reverse osmosis membranes based on cellulose derivatives such as cellulose acetate have a limited working life and may be damaged when stored in the dry state.

British Patent No. 1,270,172 describes the reaction of a polyamide, polyurea or polyurethane with liquid ethylene oxide under

pressure to form a graft copolymer. The graft copolymerisation is carried out to obtain a polyethylene oxide content in the graft copolymer of from 10 to 65% by weight. The polyamide, polyurea or polyurethane, in the form of a powder, is reacted with the liquid ethylene oxide in a closed vessel under pressure, the copolymer product is removed and from it membranes may be made by melting and pressing the product. Alternatively, a preformed membrane may be reacted with the liquid ethylene oxide to effect graft polymerisation of the ethylene oxide on the membrane. The graft polymer presumably forms a layer on the membrane surface.

According to the present invention there is provided a method of modifying the properties of a solid polymer containing carboxyl or amine groups comprising reacting said polymer with a gaseous alkylene oxide.

It is obvious that the method of the invention is applicable only to polymers which react with an alkylene oxide.

Preferably the alkylene oxide is ethylene oxide or propylene oxide.

The method of preparation of the polymers is unimportant and the reaction with the alkylene oxide may be effected with the polymers in particulate form or in the form of fibres or films.

Most preferably the polymer is in the form of a film or membrane. A convenient method of preparing a membrane is the solvent casting technique.

Membrane modification is achieved by reacting the film with ethylene oxide or propylene oxide gas. Modification alters the transport and mechanical properties and may induce membrane insolubility by crosslinking. The crosslinking stage brought about by modification has an advantage over conventional crosslinking methods in that it is a simple matter to increase the crosslinking density by repeating the modification process. The inven-

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tion obviates the need to add crosslinking agents prior to film formation or during any polymer processing stage.

The change in mechanical properties brought about by modification is of interest since by appropriate selection of polymer composition and modification conditions, mechanical properties can be improved without adversely reducing membrane sensitivity.

The final properties of the modified polymer are dependent on processing time and temperature. This fact therefore provides a means of controlling and optimising the final properties.

On reacting a gaseous alkylene oxide with polymers by the method of this invention opening of the epoxide ring occurs under the relatively mild conditions. Under atmospheric or slightly sub-atmospheric pressure, modification has been successfully carried out at temperatures ranging from 20°C to 100°C. While this temperature range can be extended, it is obvious that operation at low temperatures is of great benefit when dealing with heat-sensitive materials.

Acrylonitrile copolymers may be modified by this invention. The copolymers may be prepared by copolymerising acrylonitrile with acrylic acid, methacrylic acid, itaconic acid, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, dimethylaminoethyl acrylate or diethylaminoethyl acrylate. These acrylonitrile copolymers are best prepared by emulsion polymerisation techniques using thermal or chemical initiation. The copolymer may be recovered from the emulsion by conventional methods. The copolymer, purified by washing and drying, is dissolved in a suitable organic solvent such as dimethylformamide. A membranous sheet may then be formed by casting a solution of polymer on to a flat plate or a tubular substrate and permitting solvent to evaporate. Alternatively, membranes may be prepared on a continuous basis by casting on to a suitable release material on conventional solution casting equipment.

It is also possible to partially remove the solvent and to immerse the membrane into a suitable non-solvent, the immersion time and temperature being possible of variation.

Membrane modification is achieved by reacting the membranous sheet with, for example, ethylene oxide or propylene oxide gas. Modification alters the transport and mechanical properties and induces membrane insolubility.

Modification of acrylonitrile copolymer membranes with ethylene or propylene oxide induces two principal effects viz.

- (1) Insolubility due to crosslinking,
- (2) Alteration to membrane transport characteristics.

The occurrence of crosslinking alters the mechanical properties of the membrane, in particular, the elongation at break. Transport characteristics are altered by the replacement of hydrophilic carboxylic acid or amine groups by hydroxyl groups. Since effects (1) and (2) are due to competing reactions, modification is dependent on reaction time and reaction temperature, the temperature range is from 20°C to 100°C with 30°C, 45°C and 60°C being particularly suitable.

This invention will now be described, by way of illustration, in the following Examples.

Example 1.

An acrylonitrile copolymer was formed by an emulsion polymerisation technique from the following formulation:—

Parts by weight		
Acrylonitrile	40	
Acrylic acid	60	
Water	300	
Potassium persulphate	1.0	85
Sodium dodecyl sulphate	1.0	
Pluronic Flake F68 (Trade Mark)	0.125	

The polymerisation was carried out at a temperature from 50 to 60°C and the polymer, after recovery from the emulsion, was purified by extensive washing with water. Both acrylonitrile and acrylic acid monomers are water-soluble and so were removed from the copolymer by the washing. The purified copolymer was dried under vacuum, although both air drying and freeze drying are possible alternatives.

The prepared copolymer was dissolved in dimethylformamide (DMF) in a 3g/100ml solution. A flat membranous sheet was formed by casting the solution on to a flat surface and passing a doctor blade over the solution. The solvent was allowed to evaporate and the copolymer thus obtained in a membranous sheet form.

Using the standard procedure used normally for clinical sterilisation, the membranous sheet prepared as above was reacted with ethylene oxide gas. Pure ethylene oxide was used and the process was carried out under slightly reduced pressure at 60°C.

A comparison of the properties of unmodified and modified films is given in Table 1.

TABLE 1

	Unmodified Membrane	Modified Membrane
Solubility	soluble in dimethylformamide	insoluble
Dry Tensile Strength (kg/cm ²)	264	260
Dry Elongation at Break (%)	6.4	7.2
Wet Tensile Strength (kg/cm ²)	too weak for measurement	14
Wet Elongation at Break (%)	too weak for measurement	150
Dialysis Properties	limited removal of urea rapid removal of creatinine	urea removal improved creatinine removal reduced

Example 2.

	Parts by weight
5 Acrylonitrile	15
Dimethylaminoethyl methacrylate	85
Water	300
Potassium persulphate	1.0
10 Sodium thiosulphate	1.0
Sodium thiosulphate	1.0
Sodium dodecyl sulphate	1.0
Pluronic Flake F68 (Trade Mark)	0.25

The polymerisation was carried out at a temperature of 50°C. Polymer recovery and purification were similar to those described for Example 1. 15

The prepared copolymer was dissolved in dimethylformamide as a 10% by weight solution. A membrane was obtained by the manner described in Example 1. 20

Part of the membrane was modified by reaction with ethylene oxide for 3 hours at 30°C.

A comparison of the properties of unmodified and modified films is shown in Table 2. 25

TABLE 2

	Unmodified Membrane	Modified Membrane
Solubility	soluble in dimethylformamide	insoluble
Dry Tensile Strength (kg/cm ²)	630	600
Dry Elongation at Break (%)	4.8	4.0
Wet Tensile Strength (kg/cm ²)	58	170
Wet Elongation at Break (%)	70	140
Dialysis Properties	impermeable to urea	readily permeable to urea

Example 3.

A copolymer of acrylic acid (AA) and n-butyl methacrylate (NBMA) was prepared from a monomer weight ratio AA:NBMA of 30:70. An emulsion polymerisation initiated by potassium persulphate was employed. The reaction was carried out for 6 hours at 65 to 70°C.

The solid polymerisation product was washed, dried and dissolved in dimethylformamide at a concentration of 5g/100 ml solvent. The polymer was cast to form a membrane.

The membrane was divided into sections, some of which were processed with ethylene oxide gas at 60°C for 0.5, 1, 2, 4, 6, 8, 10, and 16 hours respectively. Modification was carried out at a slightly reduced pressure with a gas concentration in excess of 1400mg/l.

Membrane strips 2.5 cm wide and 15 cm long were taken from each section and im-

mersed in distilled water for 1 hour at 37°C. Film mechanical properties were measured on an Instron Universal Testing Instrument, Model TT—CM generally in accordance with British Standard Specification 1133: Section 21: 1964. A good summary of the results are given in Table 3.

From the results given in Table 3, the following points are of significance:

- (a) Modification gives an increased elongation at break.
- (b) processing time increases, there is a decrease in the load required to reach elongations of 5%, 10% and 15%, indicating an increase in membrane flexibility.
- (c) Membrane mechanical properties are directly dependent on modification conditions.

TABLE 3
AA-NBMA membrane reacted with ethylene oxide at 60°C:
Wet membrane mechanical properties.

Processing Time h	Load kg/cm width×10 ²				Elongation at Break %
	5% Elongation	10% Elongation	15% Elongation	Break	
0	14.6	—	—	15.3	8
0.5	17.5	18.3	19.0	22.8	51
1	13.2	14.3	15.2	20.8	55
2	8.4	10.7	12.4	20.0	54
4	7.1	9.1	10.4	17.0	56
6	5.9	7.9	9.6	16.0	55
8	5.9	7.7	9.2	16.0	57
10	5.8	7.6	8.9	16.0	63
16	4.4	5.9	7.2	19.0	89

Example 4.

A copolymer similar to that of Example 3 but having a monomer weight ratio AA:NBMA of 38:62 was prepared. A membrane, as in Example 1, was produced by solvent casting from DMF.

The membrane was divided, into four sections, one of which was left unmodified. The remaining three sections were processed with propylene oxide at 75°C for 2 hours. Modification was carried out at a slightly reduced pressure with a gas concentration in excess of 1400mg/l. One of the three samples was withdrawn and the remaining two processed with propylene oxide at 75°C for a further 2 hours. One of the two samples was withdrawn and the remaining sample processed

with propylene oxide at 75°C for a further 2 hours.

Breaking loads and elongations at break were obtained from dry film samples of all four sections. The testing procedure, as in Example 3, was generally in accordance with British Standard Specification 1133: Section 21: 1964. Results are summarised in Table 4. Results of significant interest are:

- (a) Modification greatly improves the flexibility of the dry film.
- (b) Changes in properties resulting from modification can be effectively achieved by carrying out the reaction in a stepwise manner.

TABLE 4

AA-NBMA membrane reacted with propylene oxide at 75°C:
Dry membrane mechanical properties.

Total Processing Time h	Breaking Load kg	Elongation at Break %
0	1.71	3
2	0.98	23
4	0.44	107
6	0.39	154

Example 5.

A copolymer of dimethylaminoethyl methacrylate (DMAEMA) and acrylonitrile (AN) was prepared from a monomer weight ratio DMAEMA:AN of 15:85. A redox emulsion polymerisation using sodium thiosulphate and potassium persulphate was used. The reaction was carried out for 2 hours at 50°C.

The solid polymerisation product was washed, dried and dissolved in DMF at a concentration of 10g/100ml solvent. The polymer was cast into film form with a dry thickness of 0.0006 in.

The membrane was divided into sections, some of which were treated with ethylene oxide gas in a manner similar to that described

in Example 3. Membrane sections were processed at 30°C for 2, 4, 8 and 16 hours and at 60°C, for 1, 3, 5, 8 and 16 hours respectively. The ultrafiltration characteristics of the different sections were compared by measuring water permeabilities. The results are given in Table 5.

Results of significant interest are:

- (a) Modification results in a vastly improved water permeability.
- (b) Water permeability is dependent on processing time.
- (c) Water permeability is dependent on processing temperature.

TABLE 5

DMAEMA-AN membrane reacted with ethylene oxide at 30° and 60°C:
Membrane water permeability.

Processing Temperature °C	Processing Time h	Water Permeability ml min ⁻¹ cm ⁻² Torr ⁻¹ 10 ⁶
—	0	0
30	2	1.895
	4	4.500
	8	3.317
	16	2.930
60	1	1.920
	3	3.147
	5	1.925
	8	1.705
	16	0.882

Example 6.

A copolymer of dimethylaminoethyl methacrylate (DMAEMA) and acrylonitrile (AN) was prepared from a monomer weight ratio DMAEMA:AN of 17:83. The polymerisation medium was water with sodium thiosulphate and potassium persulphate as initiators. The reaction was carried out for 2 hours at 22 to 24°C.

The solid polymerisation product was washed, dried and dissolved in DMF at a concentration of 17g/100ml solvent. The polymer was cast into film form.

The membrane was divided into two sections, one of which was treated with ethylene oxide, in a manner similar to that described in Example 3, for 3 hours at 30°C.

The blood compatibility of both sections was assessed by comparing their blood platelet retentions in a membrane testing circuit designed for this purpose [Lindsay et al., Brit. J. Haemat. 24, 377 (1973)]. Reduced blood platelet attraction is believed to enhance surface blood compatibility.

The results showed, in a statistically significant difference, that fewer blood platelets adhered to the modified membrane. The invention, therefore, provides a means of altering the blood compatibility of a polymer surface.

Example 7.

A copolymer of acrylic acid (AA) and acrylonitrile (AN) was prepared from a monomer weight ratio AA:AN of 30:70. The polymerisation medium was water with sodium thiosulphate and potassium persulphate as initiators. The reaction was carried out for 4 hours at 22 to 24°C to give a finely dispersed solid product.

The product was washed, dried and dissolved in DMF at a concentration of 3g/100ml solvent. The polymer was cast into film form.

The membrane was divided into two sections, one of which was treated with ethylene oxide, in a manner similar to that described in Example 3, for 16 hours at 60°C.

The biochemical degradation resistance of both sections was assessed by the following method:

Film strips were covered with corn steep liquor containing 1% glucose to which *Aspergillus niger* had been added and grown for 5 days. The strips were agitated on an orbital shaker at 200 rev/min for 5 days at 35°C.

The unmodified membrane disintegrated.

The modified membrane remained intact and mechanical testing, in a manner similar to that described in Example 3, indicated no significant change in breaking load had occurred as a result of contact.

A high biochemical degradation resistance is a desirable membrane property. The invention provides a means of altering the biochemical resistance of a polymer.

WHAT WE CLAIM IS:—

1. A method of modifying the properties of a solid polymer containing carboxyl or amine groups comprising reacting said polymer with a gaseous alkylene oxide.

2. A method according to claim 1, wherein the alkylene oxide is ethylene oxide or propylene oxide.

3. A method according to claim 1 or 2, wherein the polymer is in the form of a film or membrane.

4. A method according to any preceding claim, wherein the polymer is a copolymer of acrylonitrile with acrylic acid, methacrylic acid, itaconic acid, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, dimethylaminoethyl acrylate or diethylaminoethyl acrylate.

5. A method according to any one of the preceding claims, wherein the reaction is carried out at a pressure of alkylene oxide of not greater than ambient atmospheric pressure and at a temperature of from 20 to 100°C.

6. A method according to any one of the preceding claims, wherein the said method is carried out in stepwise manner to progressively modify properties of the polymer.

7. A method of modifying the properties of a polymer, according to claim 1, substantially as hereinbefore described.

8. A method of modifying the properties of a polymer according any one of the Examples.

9. A polymeric membrane whenever treated by the method claimed in any one of claims 1 to 8.

FITZPATRICKS,
Chartered Patent Agents,
Fitzpatrick House,
14—18 Cadogan Street,
Glasgow G2 6QW
— and —
Warwick House,
Warwick Court,
London WC1R 5DJ.